

PATENT ABSTRACTS OF JAPAN

(11) Publication number : 2000-268890
(43) Date of publication of application : 29. 09. 2000

(51) Int. Cl. H01M 14/00
H01L 31/04

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(54) PHOTOELECTRIC TRANSDUCER AND PHOTOSENSITIZING PIGMENT FOR
TRANSDUCER

(57) Abstract:

PROBLEM TO BE SOLVED: To provide a photoelectric transducer of photosensitizing type consisting of solid substance having an excellent photoelectric conversion efficiency capable of suppressing exfoliation of each electrode from an electric charge conveying layer and accomplishing a long lifetime of cell.

SOLUTION: This photoelectric transducer is composed of a semiconductor electrode 3a pigment 4 carried thereby and expressed by ML₁L₃L₄L₅ and/or ML₂2L₆L₇ and an electric charge conveying layer 5 including a bond with the pigment 4. In the expression for the pigment M is either of rutheniumosmium and iron L₁ and L₂ are organic ligand unsubstituted or substituted with 1-3 carboxyl radicalshydroxyl radicalssulfon radicals or cyano radicals and at least one of L₃-L₅ and also of L₆-L₇ is able to form a bond of M with the electric charge conveying layer by a coupling radical expressed by X-Y-where X is either of the hydroxyl radicalthiol radicalcarboxyl radicalphosphonic groupsulfonic group and amino radicalwhile Y is two-valent aromatic compound of C₃-30 substitution or non-substitution.

CLAIMS

[Claim(s)]

[Claim 1]Coloring matter expressed with following ML₁L₃L₄L₅ and/or ML₂₂L₆ L₇ which it was supported on a semiconductor electrode and said semiconductor electrodeand have been chemically combined with a charge transport layer via a chemical bond group [M is chosen from a rutheniumosmiumand iron among a formulaand L₁ and L₂By an organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or onetwo or three carboxyl groupshydroxyla sulfone groupand a cyano groupor three seats. Among L₃-L₅ or L₆ - L₇respectively at least one. X-Y- (X [however] -- a hydroxyl groupa thiol groupa carboxyl groupand a phosphonic acid group.) It is a substituent chosen from a group which consists of a sulfonic group and an amino groupcoordinating to the central metal M -- Y -- from divalent substitution or an unsubstituted aromatic-compounds structure of the carbon numbers 3-30 -- becoming -- an optoelectric transducer which is the bond groups expressed and is characterized by having a charge transport layer which has] chemically combined with a charge transport layer via the bond groups.

[Claim 2]ML₁L₃L₄L₅ and/or ML₂₂L₆ L₇ [M is chosen from a rutheniumosmiumand iron among a formulaand L₁ and L₂By an organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or onetwo or three carboxyl groupshydroxyla sulfone groupand a cyano groupor three seats. Among L₃-L₅ or L₆ - L₇respectively at least one. X-Y-Z (X [however] -- a hydroxyl groupa thiol groupa carboxyl groupand a phosphonic acid group.) It is a substituent chosen from a group which consists of a sulfonic group and an amino groupPhotosensitizing pigment for optoelectric transducers which it is coordinating to the central metal Mand Y consists of divalent substitution or an unsubstituted aromatic-compounds structure of the carbon numbers 3-30and is expressed with Z being a reaction group which can form a charge transport layer and a chemical bond].

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention]This invention relates to the optoelectric transducer which is related with a solid optoelectric transducerand

raised the photoelectricity energy conversion efficiency conventionallyand prevented exfoliation with a coloring matter support electrode and a charge transport layer.

[0002]

[Description of the Prior Art]As a photosensitization type solar batteryas indicated to the proceedings "solid-state dye-sensitized solar cell" of the Osaka University organicity optical engineering research center-sponsored collection "basic physical properties of a semiconductor photocatalystand application" of the 5th organicity optical engineering research center symposium gistsPolymer is combined with coloring matterit is considered as a charge transport layerand there are some which generated electricity. Herethe following methods are used by making coloring matter and a charge transport layer into the method of joining not but combining. Ruthenium coloring matter (****- 3-(pyrrole- 1-ylmethyl) pyridine- NN'-bis(22'-bipyridyl 44'-dicarboxyl acid)ruthenium (II)) is used as coloring matterElectrolytic polymerization is carried out in the solution containing pyrrole and ClO₄⁻ andsimultaneously with polypyrrrole (charge transport layer) compositioncombination with coloring matter is made. Howeverthis method also has light energy conversion efficiency as low as 1% or lessand the actual condition is not having resulted in utilization.

[0003]

[Problem(s) to be Solved by the Invention]In a wet sensitization type solar cellas indicated to the "solid-state dye-sensitized solar cell" of the Osaka University organicity optical engineering research center-sponsored collection "basic physical-properties [of a semiconductor photocatalyst]and application" proceedings of the 5th organicity optical engineering research center symposium gistsIt is also one method to carry out the chemical bond of the semiconductor electrode and solid charge transport layer to which coloring matter was made to stick. Howevversince combination is between coloring matter and a charge transport layer as compared with the time of combination not having an electronic transition since the coloring matter used here has a bad absorption feature and the long wavelength absorption feature is badin spite of being carried out at high speedThere was a problem that the photoelectricity energy conversion efficiency was decreasing or less [of a wet cell] to 1/10.

[0004]In this inventionthe problem of exfoliation with a light energy conversion efficiency fall and coloring matterand a charge transport layer when a charge transport layer which was described above is used as a solid by forming a charge transport layer and a chemical

combinationand using coloring matter also with good light absorption characteristics is solved simultaneously.

[0005]

[Means for Solving the Problem]In this inventionby a charge transport layer combining coloring matter and a charge transport layer in a solid dye sensitizing type optoelectric transducer. An electric charge which can move per unit time between a coloring matter-charge transport layer increasesand light energy conversion efficiency is highand also exfoliation between coloring matter and a charge transport layer can be preventedand an element which can solve a problem looked at by optoelectric transducer using the conventional solid charge transport layer at a stretch is provided.

[0006]Specifically combine firmly a charge transport layer and a coloring matter support electrode with a ligand of coloring matter using a ligand with a basis which can form a charge transport layer and a chemical bondand further by the ligand. In order that the optical absorption nature of coloring matter may long-wavelength-izelight energy conversion efficiency can improve by leaps and boundsand junctionlight energy conversion efficiencyand a problem of exfoliation which were problems in a solid charge transport layer until now can be solved simultaneously.

[0007]Although electronic transition of a cell indicated to the above-mentioned collection of the 5th organicity optical engineering research center symposium gists to a charge transport layer was improving rather than a time of using coloring matter without combinationthere was a problem in light energy conversion efficiency being 1/10 or less [of 1% or less and a wet cell]. As a result of our inquiring in detailwith this coloring matteras for a cause of decline in light energy conversion efficiencyit turned out that light absorption characteristics are because a falli.e.absorptionis carrying out short wavelength formation rapidly. If absorption of coloring matter falls when a complex is used for coloring matterand coloring matter and a charge transport layer are combineda cause of the fallIt thought that it was in a ligand of a side combined with a charge transport layer instead of a ligand of a side which is sticking to a semiconductor electrodeand its attention was paid to a ligand of a side combined with a charge transport layer. The kind was changed variously and the characteristic of coloring matter or a cell was evaluated. As a resultwhen the portion itself configurated in a central metal like pyridine used a molecule which has a ring structure as a ligand with a charge transport layer and combinationit turned out that the long wavelength absorption feature of coloring matter gets

worse remarkably and light energy conversion efficiency falls. on the contrary a functional group (for example a hydroxyl group a thiol group and a carboxyl group.) which carries out a coordinate bond Structure which organic molecules such as the benzene ring have combined with a phosphonic acid group a sulfonic group and an amino acid group A result of a coordination portion and a hydrocarbon portion not having a ring structure and the light absorption characteristics of coloring matter having improved by leaps and bounds and carrying out long wavelength absorption of the molecule which a skeleton of a ligand sees macroscopically and has linear structure with coloring matter used for a ligand was obtained. A result light energy conversion efficiency naturally indicates improvement in wonderful to be as a cell was brought. [0008] In a cell in which coloring matter and a charge transport layer do not have combination a volume change accompanying a phase change when impregnating with a difference and a charge transport layer of a coefficient of thermal expansion between coloring matter-charge transport layers etc. can be considered as a cause by which exfoliation breaks out between coloring matter-charge transport layers. Since it is junction only by Van der Waals force when it does not have combination molecules only adjoin and it cannot approach to sufficient distance for an electron to win popularity at high speed and to be passed. However by having combinations since molecules will be connected and it will be connected with a covalent bond an electronic transition came to be performed at high speed. An aromatic ring or a hydrocarbon portion which a portion configurated in a central metal an aromatic ring or a hydrocarbon portion has combined by 1-fold combination as a structure of coloring matter and which had a charge transport layer and combination for the ability to fold can rotate focusing on the 1-fold combination. Therefore it has the flexibility of structure as a ligand and coloring matter and exfoliation by heat stress etc. does not take place.

[0009]

[Embodiment of the Invention] When it becomes an optoelectric transducer the coloring matter (it may be hereafter called sensitizing dye) by this invention combines with a charge transport layer chemically via bond groups and is following $ML_1L_3L_4L_5$ and/or $ML_2, L_6 L_7$. [M is chosen from a ruthenium osmium and iron among a formula and L₁ and L₂ By the organic ligand of two seats respectively replaced independently by at least one sort of substituents chosen from un-replacing or one two or three carboxyl group hydroxy la sulfone group and a cyano group or three seats. Among L₃-L₅ or L₆ - L₇ respectively at least one. X-Y- (X

[however] -- a hydroxyl groupa thiol groupa carboxyl groupand a phosphonic acid group.) It is a substituent chosen from the group which consists of a sulfonic group and an amino groupcoordinating to the central metal M -- Y -- from the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30 -- becoming -- it is the bond groups expressed and is expressed with] chemically combined with the charge transport layer via the bond groups.

[0010]In the coloring matter simple substance which has not joined togetheras shown in claim 2respectively of L3-L5 or L6 - L7 at least one. [of a ligand] X-Y-Z (X [however] -- a hydroxyl groupa thiol groupa carboxyl groupand a phosphonic acid group.) It is a substituent chosen from the group which consists of a sulfonic group and an amino groupand it is coordinating to the central metal MY consists of the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30and Z has become a reaction group which can carry out a charge transport layer and a chemical bond.

[0011]By having combination with a charge transport layerfrom a charge transport layerat high speedthe coloring matter by such this invention wins popularityand comes to be passedCombination with a charge transport layer is firmand exfoliation between coloring matter-charge transport layers does not take place easilyand light absorption characteristics are goodand it is the greatest feature that the effect [conversion efficiency / light energy] wonderfully that it is high happens simultaneously.

[0012]As for sensitizing dyein order to combine with a semiconductor electrode stronglyit is preferred to have a functional group which can be adsorbed or combined by the chemical interaction on the surface of a semiconductor electrode. For exampleit is preferred to have functional groupssuch as a carboxyl grouphydroxyla sulfone groupand a cyano groupin a molecule.

[0013]sensitizing dye -- the coloring matter of 6 coordination -- it RuLa₋₃(ing)RuLb₋₂(ing) and preferablyRuLc₂L₂RuLdL₃OsLa₃With the coloring matter of 6 OsLb₂OsLc₂L₂OsLdL₃FeLa₃FeLb₂FeLc₂L₂and FeLdL₂ type coordination. It had a functional group which can have adsorption or combination in a semiconductor electrode as mentioned abovecould adsorb or combine with the semiconductor electrodeand has combined with the charge transport layer via bond groups like X-Y- of a statement further at the claim to a central metal. The ligand of the side which specifically makes the charge transport layer and combination of coloring mattergeneral formula X-Y- (X -- a hydroxyl groupa thiol groupa carboxyl groupand a phosphonic acid group.) It was chosen out of the group which consists of a sulfonic

group and an amino groupand has configurated in the central metal M and Y is the divalent substitution or unsubstituted aromatic-compounds structure of the carbon numbers 3-30By the functional group to which the electronic state of coloring matter is changed preferablyit is replaced and A more desirable substituent electron-donative in a functional groupFor exampleit is important to use the ligand which the coordination portion which can be expressed in writing by -O-R-N-RCOORCONR₂COR (R is an alkyl group)etc. and one-fold aromatic ring portion have combined. Y A phenylene derivativea phenylenevinylene derivativea biphenylene derivativeA thiophene derivative etc. are preferred and the structure containing hydroxymethylepoxy groupssuch as halogenation methyl allyl groupssuch as a chloromethyl phenyl groupand a hydroxy methylphenyl groupa thiophene derivativea pyrrole derivativean aniline derivativeetc. is good.

[0014]If such coloring matter is usedan adhesive property with a semiconductor electrodea charge transport layerand each improvesit can become possible to prevent exfoliation by a thermal excursion etc. etc. and the endurance of a solar cell can be raised. Depending on the ligand portion combined with the charge transport layerthis will have the structure where a molecule is soft because between the coordination portion to the central metal of coloring matter and structures with an aromatic ring or conjugate has 1-fold combinationand neither decomposition nor secession will take place between the coloring matter-charge transport layers by stress. The light absorption characteristics of the coloring matter using the ligand of such a structure are improving by leaps and boundsand since the charge transfer from a charge transport layer to coloring matter becomes as [perform / charge transfer / at high speed and smoothly]it becomes possible to raise light energy conversion efficiency of them substantially. Coloring matter could have combination with coloring matterand should just be eventually connected with combination with firm above coloring matter and charge transport layers. A desirable optoelectric transducer has coloring matter in which the ligand portion combined with the charge transport layer of coloring matter and the charge transport layer are carrying out conjugateand a charge transport layer by this invention.

[0015]A charge transport layer receives an electron from the counter electrode surface at leastand it consists of the career supporting material or carrier conductivity material which serves to return the coloring matter which became trivalent by passing coloring matter to divalent. An electronor a hole or ion may be sufficient as the career which moves in the inside of a charge transport layer. As for ionthe

ionic species in which oxidation reduction is possible are used reversibly. Such materials which constitute a charge transport layer are illiquid and the thing of the gel state or a solid state is used.

[0016] As for a charge transport layer as shown below every material has coloring matter and combination eventually. As bond groups when coloring matter and a charge transport layer have combination Carbon-carbon bonding a carbon-oxygen bond C-N-C-Si-Si-O-etc. are preferred from a point of bond strength for example a methylene group an ether bond a thioether bond an ester bond an amide bond imide bonding a siloxane bond etc. are raised. It is desirable to choose especially bond groups in which a charge transport layer carries out conjugate to a ligand in the case of a hole transportability layer.

[0017] When a career is ionas a material system which constitutes a charge transport layer 1. solid electrolyte materials 2. gel electrolyte material 3. fused salt electrolyte material etc. can be used good.

[0018] 1. As solid electrolyte material the ionic species in which oxidation reduction is possible and the mixture of an ion-conductive high molecular compound are used reversibly. Especially if oxidation reduction is reversibly possible for ionic species will not be limited but. For example the ion (I^-/I^{3-}) of iodine the ion (Se^{2-}/Se_2^{2-}) of selenium ion (Te^{2-}/Te_2^{2-}) of a tellurium ferro cyanogen / FERI cyanide ion $[Fe(CN_6)]^{4-}/[Fe(CN_6)]^3-$ Ionic species such as cyano complexes of metals such as tungsten and molybdenum $H_3PO_2^-$ and $S_2O_4^{2-}$ are mentioned. As an ion-conductive high molecular compound polar high molecular compound such as for example polyetherpolyesterpolyamine and polysulfide are used.

[0019] 2. As a gel electrolyte material the ionic species in which oxidation reduction is possible and the thing ** constituted are used for ** polar organic solvent ** gelling agent and ** reversible target good. ** A polar organic solvent will not be limited especially if the ionic species of ** are dissolved good but it is preferred that it is an aprotic organic solvent. For example ester species such as acetonitrile ethylene carbonate propylene carbonate lactone or the mixture of those can be considered. ** As a gelling agent a polymers gelling agent is used good. For example polymers gelling agents such as polymer which has nitrogen-containing heterocyclic quaternary compound salt structure etc. are used for a cross-linked-poly acrylic resin derivative a cross-linked-poly acrylonitrile derivative a polyalkylene oxide derivative or silicone resin and a side chain. ** As ionic species in which oxidation reduction is possible the same ionic species can be used reversibly as the paragraph of 1. solid electrolyte described.

[0020] 3. What the molten salt electrolysis liquid which the ionic

species in which oxidation reduction is possible dissolved in ordinary temperature type fused salt reversibly was gelling by the gelling agent as a fused salt gel electrolyte material or the ordinary temperature type fused salt in which oxidation reduction is possible gelled by the gelling agent is used. It can be with the ionic species reversibly same as ionic species in which oxidation reduction is possible as the paragraph of 1. solid electrolyte described. As ordinary temperature type fused saltnitrogen-containing heterocyclic quarternary-ammonium-salt compoundssuch as pyridinium salts and imidazolium saltsare used good. The above nitrogen-containing heterocyclic quarternary-ammonium-salt compounds which use as an opposite anion the ionic species reversibly same as fused salt in which oxidation reduction is possible as the paragraph of 1. solid electrolyte described are used. The same polymers gelling agent can be used as a gelling agent as the paragraph of 2. gel electrolyte material described. It is good also considering the high molecular compound which furthermore has nitrogen-containing heterocyclic quarternary-ammonium-salt structure as a side chain as a gelling agent.

[0021]As a solid hole or an electronic transition materialthe high molecular compound which has the organic low molecular weight compoundthese holesor electron-transport-property molecular structure of crystallinity or amorphous nature in a side chain or a main chaina conjugate property high molecular compoundetc. are used. As a hole or an electron-transport-property compoundas what has crystallinityfor exampleelectron donor acceptor complexessuch as a polycyclic aromatic derivative and tetrathiafulvalenesuch as various metal-phthalocyanines derivativesperylene tetracarboxylic acidperylene and coronenesand tetracyano quinodimethanesetc. can be mentioned -- as an amorphous material -- for example [0022]

[Formula 1]

It comes out and an aluminium compounddiaminevarious ONISA diazole derivativesetc. which are shown are mentioned. As a high molecular compound which has a hole or electron-transport-property molecular structure in a side chain or a main chainit has the hole or electron-transport-property molecular structure mentioned above in a side chain or a main chainand poly-N-vinylcarbazole is mentioned. As a conjugate property high molecular compoundconductivitysuch as a polypyrrole derivativea polyacetylene derivativea polynaphthene derivativea polythianaphthene derivativepoly anilinepolyphenylenespolyphenylene

vinyleneand polysilaneor semiconductor nature polymers are mentioned.

[0023]The transparent substrate used by this invention should just be a transparent materialfor exampleglassa polymer filmetc. are mentioned.

[0024]A transparent conductive layer is transparentand if an electrode surface is material with conductivityit is [anything] goodfor exampleits tin oxidezinc oxideetc. which doped fluorideindiumaluminumetc. are preferred. As long as it is a minute amount of a grade which seldom interrupts light transmissionan opaque metal layerfor exampleplatinumgoldsilveraluminumcopperetc. may be contained.

[0025]It is [anything] good if it is a conductive high material as a counter-electrode. It does not matter even when it is transparent and opaque. Material is electrochemically stableand its conductive high material is preferredfor exampleit can consider metalsuch as platinumgoldsilvercopperand aluminumgraphitethe above-mentioned transparent conductive layeretc.

[0026]The material used as a semiconductor electrode should just be a semiconductor with little optical absorption of a light rangeIn a metal oxide semiconductoran oxide of a transition metalfor exampletitanium zirconiumHafniumstrontiumzincindiumyttrium lantervanadiumniobiumtantalumchromiummolybdenumoxides of tungsten and these multiple oxidesor an oxide mixture is preferred. Perovskites like SrTiO₃,CaTiO₃,BaTiO₃,MgTiO₃and SrNb₂O₆these multiple oxides or an oxide mixtureGaNetc. can be used good.

[0027]A method of producing a semiconductor electrode applies on a substrate a paste which distributed particles of semiconductor electrode material in a solventGaseous phase methodssuch as the applying method for drying and calcinatinga sol gel process and a CVD method which use an alkoxide for a raw material and make a dipping spin coat etc. itand weld slagan anode oxidation methoda method of producing an oxide by a solvent interfaceetc. can be considered.

[0028]In order to adsorb more sensitizing dyethe one of a semiconductor electrode where surface area is larger is preferreda roughness factor (Rf: thing [as opposed to / thing / an unit area of a substrate] of surface area of an oxide semiconductor which was measured by gas adsorption and a surface area measuring instrument by mercury pressure ON etc.) -- at least 20 or more -- I hope preferably that there are 1000 or more still more preferably 100 or more. In order to enlarge surface areaor in order to change a surface state and to enable it to adsorb more coloring matterwhen producing a thin film a mold may be usedor etchingacid alkali treatmentetc. may be performed after thin film production. At the time of thin film productionadd organic polymer beads

etc. it is made to disperse in the case of thin film heat treatmentand porous structure may be produced.

[0029]Although it is preferred that it is a crystal as for a semiconductor materialevn when it is amorphous in partit does not matter even when it is altogether amorphous. There may be an oxygen deficiency.

[0030]In order that a transparent electrode here or a semiconductor electrode may not reduce light volume which reaches coloring matterthey have the character which penetrates light of a visible light wavelength areaand are what is penetrated not less than 70% more preferably 50% at least 30% about 300 to 800-nm light.

[0031]A cell is preferably producible as follows. A transparent electric conductor layer is provided in a transparent substrate by weld slagCVDetc. and the above-mentioned semiconductor electrode is produced on it. Although any above-mentioned method may be sufficient as a manufacturing methodelectric conductivity of a semiconductor electrode is high and it is preferred to have bolus body structure with large surface area. Although the semiconductor electrode surface is made to support coloring matterit is preferred to evaporate excess water to some extent in that case. For a certain reasonthat to which decomposition of coloring matter takes place with moisture is [a semiconductor electrode board] also good to carry out heat treatment etc. before coloring matter adsorptionand to reduce a moisture content in an electrode. How to perform simultaneously combination with production and coloring matter of a charge transport layerand a charge transport layer for a charge transport layer by electrolytic polymerization etc. after adsorption to a semiconductor electrode of coloring matter and a method of combination with coloring matter and a charge transport layer make ** coloring matter stick to a semiconductor electrode** After making coloring matter stick to a semiconductor electrode and applying charge transport layer materialhow to make react with light or heat and combinea method of combining with ** coloring matter a molecule which constitutes a charge transport layer beforehandand making coloring matter with the charge transport nature child stick to a semiconductor electrodeetc. can be considered.

[0032]** A time of using conjugate property polymers for a charge transport layer as a methodetc. can be considered. Add a reaction group to a ligand of a side first combined with a charge transport layer of coloring matterthe reaction group and a monomer of a substance to use as polymers are made to reactand coloring matter in which a monomer is given to the point of a ligand is produced. Coloring matter is made to

stick to the semiconductor electrode surface by dissolving coloring matter with a monomer which was made such and produced in an organic solvent immersing a semiconductor electrode in the solution and flowing back preferably. Electrolytic polymerization of this coloring matter support semiconductor electrode is dipped and carried out into a solution which melted a monomer and a supporting electrolyte of a charge transporting material to an organic solvent.

[0033]** Make coloring matter in which a reaction group was added to a ligand of a side combined with a charge transport layer as a method stick to a semiconductor electrode. A semiconductor electrode may be immersed in an organic solvent which dissolved coloring matter as an adsorption method and it may flow back preferably. Thus on a produced coloring matter support semiconductor electrode a charge transporting material (if required catalyst of a radical generator etc.) which dissolved in a solid state or a solution is applied and it is made to react or gel by heat or light after desiccation.

[0034]** Produce coloring matter which is combined with a charge transport nature child who shows electrical conduction and make such coloring matter adsorb on a semiconductor electrode in a method. An adsorption method dissolves coloring matter in an organic solvent etc. and is made to adsorb by making a semiconductor electrode immersed into the solution. Under the present circumstances it may flow back.

[0035]A cell is formed by providing an electrode in a coloring matter support electrode with a charge transport layer and combination which were produced as mentioned above.

[0036]Since a loss will become large while passing along a charge transport layer if distance between two electrodes is large when a cell is used if electrodes do not contact the smaller possible one of inter electrode distance is good.

[0037]What is necessary is just to measure a short-circuit current in order to know electron transfer efficiency between coloring matter and a charge transport layer. An electron will flow even through a semiconductor electrode from coloring matter efficiently so that a current value is large. An initial value was compared with a value after prolonged use for this measured value and a desquamative state was judged. It will be thought that it has exfoliated if it seems that it is falling. Light energy conversion efficiency can be easily drawn with a parameter in a formula of the following measured when it irradiated with sunlight (AM1.5).

As for short circuit current density and $V_{oc}\eta_{global} = (i_{ph} \times V_{oc} \times ff) / I_s \eta_{global}$ is [light energy conversion efficiency and i_{ph} / a fill factor and I_s of

open circuit voltage and ff] the intensity of irradiation light.

[0038]

[Example] Although an embodiment of the invention is described below this invention is not limited to this example.

[0039] [Example 1]

1) After adding 21 ml of nitric acid to 5 g of production titanium dioxide ultrafine particles (mean particle diameter of 14 nanometers anatase) of the titanium dioxide layer and fully agitating 3.5 g of polyethylene glycols were added and agitated and the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visually among the air at 440 ** it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours[0040]

[Formula 2]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure in the 0.15M isothianaphthene containing 0.1MLiClO₄ and acetonitrile fluid with constant potential (vs. Ag/Ag⁺) photoelectrical depolymerization of the thianaphthene was carried out and the polythianaphthene layer was formed. Under the present circumstances it was checked that the coloring matter support titanium dioxide thin film had been thoroughly covered with the polythianaphthene layer. The thickness of the polythianaphthene single layer could be 10 microns.

4) Sealing resin is applied to the surroundings of the coloring matter support titanium dioxide thin film produced by the production 3 of the cell and the titanium oxide membrane of the substrate of polyisothianaphthene. The glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was stuck by pressure by hot

pressingsealing resin was solidifiedand the cell of this invention was produced.

5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0041][Example 2]

1) Clean ultrasonically in ethanol the glass substrate in which the conductor layer of the tin oxide which carried out the production fluoride dope in CVD of a barium titanate layer is providedand use it as a substrate. A raw material is barium. Using beta-diketonate bis(dipivaloyl meta-NATO)barium and titanium isopropoxideit was made to evaporate at 200 ** and 60 **respectivelyand membrane formation was performed for 4 hours by the substrate temperature of 600 **the total pressure of 10 torrsand 2 torrs of oxygen pressure.

2) Adsorption to barium titanate of coloring matter[0042]

[Formula 3]

It comes out30 mg of shown coloring matter is dissolved into the ethanol which carried out dehydrating treatmentand the semiconductor electrode board produced by 1 is made immersed into the solution for 5 hours.

After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

The joint iodine tetrabutylammonium salt of a charge transport layer and coloring matter 3) 10 mgAs 5 mg and a radical generatorazobisisobutironitoriru is dissolved in 2 mg70 mg of poly (ethylene glycol) dimethacrylate ($M_w=600$) is dissolved in 1-ml THFand an iodine is applied to the substrate with a semiconductor electrode produced by 2and is dried with a dryer.

4) The bead of 10-micron polydivinylbenzene was uniformly bound as a spacer on the coloring matter support titanium dioxide thin film board produced by the production 2 of the cellthe glass substrate in which the tin oxide thin film of the fluoride dope was provided was piled upit left the electrolyte injected holeand the circumference was closed with the epoxy resin. From an injected hole [Iodination tetrapropylammonium] = 0.5M[Potassium iodide] = 0.02M[I₂] The acetonitrile / ethylene

carbonate mixed solution of 0.03M (capacity factors 10/90) = 90 weight sectionsThe mixed liquor of poly (ethylene glycol) diacrylate ($M_w=600$) 8.5 weight sectionTOKIKAHIRORU pro pantry acrylate 0.5 weight sectionand azobisiso CHIRONI tolyl (azobisisobutironitoriru) 1 weight section was poured in. The injected hole was sealed with the epoxy resin after pouring. After sealingit heated for 10 hours and 60 ** of cells of this invention were produced.

5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0043][Example 3]

1) After adding 25 ml of nitric acid to 8 g of production strontium titanate (mean particle diameter of 50 nanometers) of the strontium titanate layer and fully agitating4 g of polyethylene glycols were added and agitatedand the dispersion liquid of strontium titanate were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visuallyamong the airat 500 **it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the strontium titanate of coloring matter at 120 ** for 2 hours[0044]

[Formula 4]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

3) Combination with a charge transport layer and coloring matterand production of a cell [1-methyl-3-ethyl-imidazolium iodide] = 0.5M $[I_2]$ = the 1-methyl-3-ethyl-imidazolium of 0.05M -- doria -- a rate solution 90 weight sectionsPoly (ethylene glycol) diacrylate ($M_w=600$) 8.5 weight sectionThe mixed liquor of trimethylolpropane triacrylate 0.5 weight

section and azobisisobutironitoriru 1 weight sectionIt applied to the substrate produced by 2) the glass substrate which wound the spacer uniformly and provided the tin oxide conductive layer which carried out the fluoride dope was piled upthe circumference was closed with the epoxy resinand the hotpress was carried out at 100 ** for 30 minutes. 4) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0045][Example 4]

- 1) Prepare 29 g of production ** titanium tetraisopropoxide of a titanium dioxide layer19 g of drying ethanol and 18 g of ** drying ethanolthe pure water 1.8gand two kinds of solutions of 35%HCl solution 3g**add every to **agitate a little ** to itand produce sol. Carry out the spin coat of the prepared soland irradiate with ultraviolet rays desiccation and after thatand it is made to crystallize on the polymethylpentene board which provided the ITO filmand is considered as titanium oxide membrane.
- 2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours[0046]

[Formula 5]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

- 3) On the coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter20 ml of acetonitrile10 mg of methyl methacrylate7 mg of iodine tetrabutylammonium saltsand optical radical generator (0.5 mg of trimethylolpropane triacrylate1 mg of methylbenzo IRUFO mates) mixed liquor are appliedand it is made to dry with a dryer. The bead of 10-micron divinylbenzene is uniformly bound as a spacer on itin pileswith the bottom mercury-vapor lamp of argon gas atmospherethe optical

exposure was carried out and photo-curing of the polymethylpentene board which provided the ITO film was carried out.

4) It took out in the cell produced by the evaluation 3 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0047] [Example 5]

1) After adding 18 ml of nitric acid to 3 g of production niobium pentoxide ultrafine particles (mean particle diameter of 70 nanometers) of the niobium pentoxide layer and fully agitating3.5 g of polyethylene glycols were added and agitatedand the dispersion liquid of niobium pentoxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visuallyamong the airat 600 **it calcinated for 45 minutes and cooled to the room temperature.

2) After reheating among the air the niobium pentoxide layer produced by the adsorption 1 to niobium pentoxide of coloring matter at 120 ** for 2 hours[0048]

[Formula 6]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown coloring matter into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support niobium pentoxide thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0049]

[Formula 7]

It comes out and 10 mg of hole conductors and azobisisobutironitorirulmg which is shown are dissolved in 30 ml of acetonitrileit applies to the coloring matter support electrode produced by 2it is driedthe glass substrate in which the tin oxide conducting film which carried out the fluoride dope was provided is piled upand a hotpress is carried out at 100 ** for 1 hour.

4) It took out in the cell produced by the evaluation 3 of the cellthe electrode was attachedand the light energy conversion efficiency which irradiated with sunlight was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0050] [Example 6]

1) After adding 21 ml of nitric acid to 5 g of production titanium dioxide ultrafine particles (mean particle diameter of 14 nanometersanatase) of the titanium dioxide layer and fully agitating3.5 g of polyethylene glycols were added and agitatedand the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visuallyamong the airat 460 **it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours[0051]

[Formula 8]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposureWithin isoindole of 0.15M containing 0. 1MLiClO₄and acetonitrile fluidwith constant potential (vs. Ag/Ag⁺)photoelectrical depolymerization of the isoindole was carried out and the poly isoindole layer was formed. Under the present circumstancesit was checked that the titanium dioxide layer had been thoroughly covered with the poly isoindole layer. The thickness of the poly isoindole single layer could be 10 microns.

4) Sealing resin was applied to the surroundings of the production titanium oxide membrane of a cellthe glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was setit was

stuck by pressure by hot pressingand sealing resin was solidified.
5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0052][Example 7]

1) After adding 24 ml of nitric acid to 6 g of production strontium titanate ultrafine particles (mean particle diameter of 100 nanometers) of the strontium titanate layer and fully agitating3.5 g of polyethylene glycols were added and agitatedand the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visuallyamong the airat 500 **it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the strontium titanate layer produced by the adsorption 1 to the strontium titanate of coloring matter at 120 ** for 2 hours[0053]

[Formula 9]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support strontium titanate thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0054]

[Formula 10]

Come out and 10 mg of hole conductors and BTTB 1mg which is shown are dissolved in 3 ml of acetonitrileIt applies to the coloring matter support electrode produced by 2)it is driedthe glass substrate which wound a 10-micron spacer and in which the tin oxide conducting film which carried out the fluoride dope was provided is piled upand a hotpress is carried out for 5 minutes at 200 **.

4) It took out in the cell produced by the evaluation 3 of the cellthe

electrode was attached it irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0055] [Example 8]

- 1) Prepare 29 g of production ** titanium tetraisopropoxide of a titanium dioxide layer 19 g of drying ethanol and 18 g of ** drying ethanol the pure water 1.8 g and two kinds of solutions of 35% HCl solution 3g ** add every to ** agitate a little ** to it and produce sol. The spin coat of the sol adjusted on the glass substrate which provided the tin oxide which carried out the fluoride dope is carried out heat treatment is carried out at 600 ** desiccation and after that for 30 minutes and it is considered as titanium oxide membrane.
- 2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours [0056]

[Formula 11]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatment it was made to dry under a nitrogen atmosphere and the coloring matter support titanium dioxide thin film was prepared.

- 3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposure Within the 0.15M isothianaphthene containing 0.1M LiClO₄ and acetonitrile fluid with constant potential (vs. Ag/Ag⁺) photoelectrical depolymerization of the thianaphthene was carried out and the polythianaphthene layer was formed. Under the present circumstances it checked that the titanium dioxide layer was thoroughly covered with polyisothianaphthene. The thickness of the polyisothianaphthene single layer could be 10 microns.
- 4) Sealing resin is applied around titanium oxide membrane on the coloring matter support titanium dioxide thin film produced by the production 3 of the cell and the substrate of polythianaphthene After setting the glass substrate which has the tin-oxide electric conduction thin film which doped fluoride and being stuck by pressure by hot

pressingthe weight was put and sealing resin was solidified every 10 hours.

5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0057] [Example 9]

1) 0.01 mol of production ** metal barium and 40 mol of isopropanols of a barium titanate layer0.03 mol of ** pure water0.7 mol of acetic acid30 mol of isopropanols** Three kinds of solutions of 0.01 mol of titanium isopropoxide and 35 mol of isopropanol ** are preparedit adds every to ** and agitate a little ** to itnext add 2000 mol of acetylacetonesagitate in 80 ** nitrogen for 2 hoursand consider it as a transparent solution. ** is added in the solution and sol is produced. Carry out the spin coat of the sol adjusted on the polymethylpentene board which provided the ITO filmand irradiate with ultraviolet rays desiccation and after thatand it is made to crystallizeand is considered as a barium titanate film.

2) After reheating among the air the barium titanate layer produced by the adsorption 1 in the barium titanate layer of coloring matter at 120 ** for 2 hours[0058]

[Formula 12]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of shown sensitizing dye into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support barium titanate thin film was prepared.

3) Combination with a charge transport layer and coloring matter [0059]
[Formula 13]

It comes out and 10 mg of hole conductors and azobisuisobutironitorirulmg which is shown are dissolved in 1 ml of acetonitrileit applies to the coloring matter support electrode produced by 2it is driedthe glass substrate in which the tin oxide conducting

film which carried out the fluoride dope was provided is piled upand a hotpress is carried out at 100 ** for 1 hour.

4) It took out in the cell produced by the evaluation 3 of the cellthe electrode was attachedand the light energy conversion efficiency which irradiated with sunlight was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0060] [Example 10]

1) After adding 21 ml of nitric acid to 5 g of production titanium oxide ultrafine particles (mean particle diameter of 14 nanometersanatase) of the titanium dioxide layer and fully agitating3.5 g of polyethylene glycols were added and agitatedand the dispersion liquid of the titanium dioxide were produced. After making it dry with a dryer until it applied on the glass substrate which has a conducting film of the tin oxide which doped fluoride for these dispersion liquid and became transparent visuallyamong the airat 460 **it calcinated for 40 minutes and cooled to the room temperature.

2) After reheating among the air the titanium dioxide layer produced by the adsorption 1 to the titanium dioxide of coloring matter at 120 ** for 2 hours[0061]

[Formula 14]

It was immersed in the coloring matter solution which came out and dissolved 30 mg of sensitizing dye shown into 100 ml of ethanol solutions which carried out dehydrating treatment for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand the coloring matter support titanium dioxide thin film was prepared.

3) The coloring matter support titanium dioxide thin film produced by the combination 2 with a charge transport layer and coloring matter under a visible light exposureWithin isoindole of 0.15M containing 0.1MLiClO₄and acetonitrile fluidwith constant potential (vs. Ag/Ag⁺)photoelectrical depolymerization of the isoindole was carried out and the poly isoindole layer was formed. Under the present circumstancesthe titanium dioxide layer checked that it had been thoroughly covered with the poly isoindole layer. The thickness of the poly isoindole single layer was 10 microns.

4) Sealing resin was applied to the surroundings of the production

titanium oxide membrane of a cellthe glass substrate which has the tin-oxide electric conduction thin film which doped fluoride was setit was stuck by pressure by hot pressingthe weight was putand sealing resin was solidified every 10 hours.

5) It took out in the cell produced by the evaluation 4 of the cellthe electrode was attachedit irradiated with sunlightand light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performedand measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0062] [Comparative examples 1-10]

1) each production of a semiconductor electrode layer -- as for the comparative examples 3-10 as well as [the comparative example 2] Example 2the comparative example 1 produced the substrate with a semiconductor electrode respectively like Examples 3-10 like the method of producing Example 1.

2) 0.001 mol of sensitizing dye shown by adsorption following (a) - (j) to the semiconductor electrode of coloring matter was dissolved into 100 ml of ethanol solutions which carried out dehydrating treatment. After reheating among the air the semiconductor electrode layer produced by 1) at 120 ** for 2 hoursthe semiconductor electrode was immersed in the coloring matter solution for 5 hours. After washing this by the ethanol which carried out dehydrating treatmentit was made to dry under a nitrogen atmosphereand coloring matter support semiconductor membrane was prepared.

[0063]In the comparative example 1the compound which shows by (h) according to (g) and the comparative example 8is shown by (i) according to the comparative example 9and is shown [the comparative example 10] by (j) according to (e) and the comparative example 6 at (f) and the comparative example 7 was used by (d) and the comparative example 5 by (c) and the comparative example 4 according to (a) and the comparative example 2 at (b) and the comparative example 3.

[0064]

[Formula 15]

[0065]

[Formula 16]

[0066]
[Formula 17]

3) To the coloring matter support titanium dioxide thin film produced by being impregnated of a charge transport layer and the production 2 of the cell. At the comparative example 1 it is 1 millimol ***** about the charge transport layer which consists of a compound of (**) and comparative example (**) by (o) and the comparative example 9 by (n) and the comparative example 8 according to (l) and the comparative example 6 in (k) and the comparative example 5 at (m) and the comparative example 7. The charge transport layer of the comparative examples 2-4 is the respectively same substance as the substance of Examples 2-4 and its manufacturing method is also the same.

[0067]
[Formula 18]

[0068]
[Formula 19]

A hotpress is carried out after pulling to a vacuum together with a coloring matter support electrode as a charge transport layer is inserted the same substrate with an electrode of a substrate as the time of producing a semiconductor electrode respectively. Around the back substrates sealing resin is applied and it is made to dry and is considered as a cell.

4) It took out in the cell produced by the evaluation 3 of the cell the electrode was attached and irradiated with sunlight and light energy conversion efficiency was measured. The short-circuit current was measured and the jointing condition was evaluated. Continuous use for one more week was performed and measurement of light energy conversion efficiency and a short-circuit current were measured. The result is shown in the following table 1.

[0069]
[Table 1]

[0070]
[Effect of the Invention] By this invention the solid sensitization type

optoelectric transducer which has photoelectric conversion efficiency equivalent to the sensitization type solar cell of the conventional wet type was obtained fast improve efficiency and exfoliation of an electrode and a charge transport layer were suppressed as compared with the conventional solid sensitization type solar cell and reinforcement of the cell was realized.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] The schematic diagram showing the section of the solar cell which is one example of the optoelectric transducer by this invention.

[Description of Notations]

- 1 Transparent substrate
 - 2 Transparent electrode
 - 3 Semiconductor electrode
 - 4 Coloring matter (thing with combination with a charge transport layer)
 - 5 Charge transport layer (thing with combination with coloring matter)
 - 6 Counter-electrode
 - 7 Substrate
-